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ON-SITE MANUFACTURE OF ULTRA-HIGH-PURITY NITRIC ACID FOR SEMICONDUCTOR PROCESSING

Abstract:

A system and method for semiconductor manufacture using on-site distillation to obtain ultra pure nitric acid from technical grade startin
3d2
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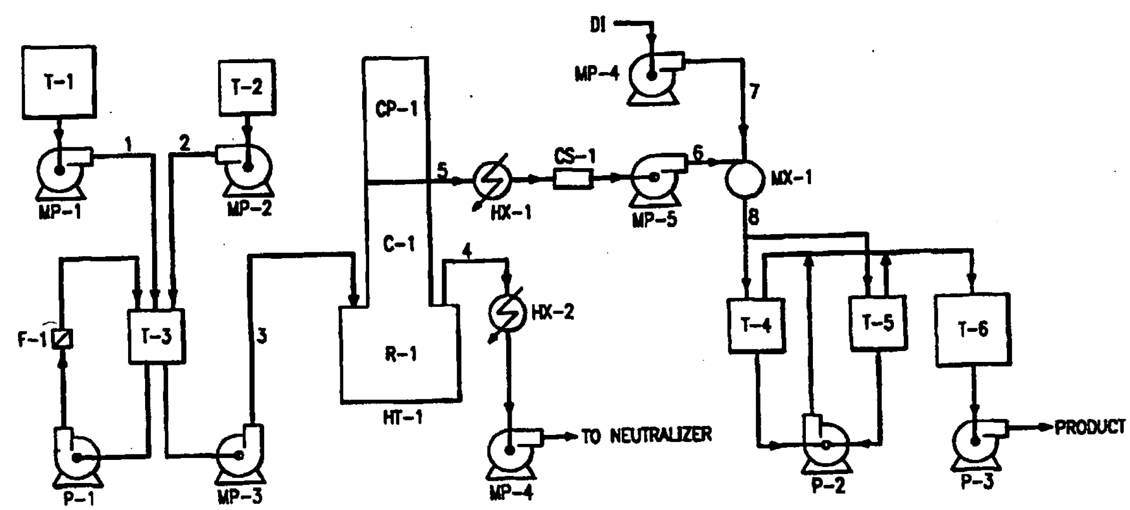
(54) Title: ON-SITE MANUFACTURE OF ULTRA-HIGH-PURITY NITRIC ACID FOR SEMICONDUCTOR PROCESSING



(57) Abstract

A system and method for semiconductor manufacture using on-site distillation to obtain ultra pure nitric acid from technical grade starting material. The source material for distillation (T-3) is provided at a concentration higher than that of the high boiling point azeotrope, so that dilution does not occur during condensation (C-1). A reflux condenser (CD-1) is used, with a purge of at least 5 % to prevent impurities from accumulating. This is performed on site, at a semiconductor manufacturing facility and the ultrapure chemical thus generated is routed directly, through ultraclean piping, to the point of use in a semiconductor front end (T-5).

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On-Site Manufacture of Ultra-High-Purity Nitric Acid for Semiconductor Processing

BACKGROUND AND SUMMARY OF THE INVENTION

The present invention relates generally to semiconductor processing, and particularly to preparation of ultrapure liquid reagents.

Background: Contamination Control

Contamination is generally an overwhelmingly important concern in integrated circuit manufacturing. A large fraction of the steps in modern integrated circuit manufacturing are cleanup steps of one kind or another; such cleanup steps may need to remove organic contaminants, metallic contaminants, photoresist (or inorganic residues thereof), byproducts of etching, native oxides, etc.

As of 1995 the cost of a new front end (integrated circuit wafer fabrication facility) is typically more than a billion dollars ($1,000,000,000), and a large fraction of this cost is directed to measures for particulate control, cleanup, and contamination control.

One important source of contamination is impurities in the process chemicals. Since the cleanups are so frequent and so critical, contamination due to cleanup chemistry is very undesirable.

Background: Wet versus Dry Processing

One of the long-running technological shifts in semiconductor processing has been the changes (and attempted changes) between dry and wet processing. In dry processing, only gaseous or plasma-phase reactants come in contact with the wafer. In wet processing, a variety of liquid reagents are used for purposes such as etching silicon dioxide or removing native

oxide layers, removing organic materials or trace organic contaminants, removing metals or trace organic contaminants, etching silicon nitride, etching silicon.

Plasma etching has many attractive capabilities, but it is not adeq[illegible] for cleanup. There is simply no available chemistry to remove some of the most undesirable impurities, such as gold. Thus wet cleanup processes are essential to modern semiconductor processing, and are likely to remain so for the foreseeable future.

Plasma etching is performed with photoresist in place, and is not directly followed by high-temperature steps. Instead the resist is stripped, and a cleanup is then necessary.

The materials which the cleanup must remove may include: photoresist residues (organic polymers); sodium; Alkaline earths (e.g. calcium or magnesium); and heavy metals (e.g. gold). Many of these do not form volatile halides, so plasma etching can't carry them away. Cleanups using wet chemistries are required.

The result of this is that purity of process chemicals at plasma etching is not as critical, since these steps are always followed by cleanup steps before high-temperature steps occur, the cleanup steps can remove dangerous contaminants from the surface before high-temperature steps drive in these contaminants. However, purity of the liquid chemicals is much more critical, because the impingement rate at the semiconductor surface is typically a million times higher than in plasma etching, and because the liquid cleanup steps are directly followed by high-temperature steps.

However, wet processing has one major drawback, namely ionic contamination. Integrated circuit structures use only a few dopant species (boron, arsenic, phosphorus, and sometimes antimony) to form the required p-type and n-type doped regions. However, many other species are electrically active dopants, and are highly undesirable contaminants. Many of these contaminants can have deleterious effects, such as increased junction leakage, at concentrations well below $10^{13}cm^{-3}$. Moreover, some of the less desirable contaminants segregate into silicon, *i.e.* where silicon is in contact with an aqueous solution the equilibrium concentration of the contaminants will be higher in the silicon than in the solution. Moreover, some of the less desirable contaminants have very high diffusion coefficients, so that introduction of such dopants into any part of the silicon wafer will tend to allow these contaminants to diffuse throughout, including junction locations where these contaminants will cause leakage.

Thus all liquid solutions which will be used on a semiconductor wafer should preferably have extremely low levels of all metal ions. Preferably the concentration of all metals combined should be less than 300 ppt (parts per trillion), and less than 10 ppt for any one metal, and less would be better. Moreover, contamination by both anions and cations must also be controlled. (Some anions may have adverse effects, *e.g.* complexed metal ions may reduce to mobile metal atoms or ions in the silicon lattice.)

Front end facilities normally include on-site purification systems for preparation of high-purity water (referred to as "DI" water, *i.e.* deionized water). However, it is more difficult to obtain process chemicals in the purities needed.

Background: Purity in Semiconductor Manufacturing

The extreme purity levels required by semiconductor manufacturing are rare or unique among industrial processes. At such extreme purity levels, handling of chemicals is inherently undesirable (though of course it cannot be entirely avoided). Exposure of the ultrapure chemical to air (particularly in an environment where workers are also present) must be minimized. Such exposure risks introduction of particulates, and resulting contamination. Shipment of ultrapure chemicals in closed containers is still not ideal, since there is inherently a higher risk of contaminants at the manufacturer or at the user's site. Moreover, undetected contamination may damage an expensively large quantity of wafers.

Since many corrosive and/or toxic chemicals are commonly used in semiconductor processing, the reagent supply locations are commonly separated from the locations where front-end workers are present. Construction and maintenance of piping for ultra-high-purity gasses and liquids are well-understood in the semiconductor industry, so most gasses and liquids can be transported to wafer fabrication stations from anywhere in the same building (or even in the same site).

The present application discloses systems and methods for preparation of ultrapure chemicals on-site at a semiconductor manufacturing facility, so that they can be piped directly to the points of use. The disclosed systems are very compact units which can be located in the same building as a front end (or in an adjacent building), so that handling is avoided.

On-Site Ultrapurification

The present inventors have developed a method for preparing ultra-high-purity liquid reagents (including aqueous HF, HCl, NH_4OH, NH_4F, and HNO_3) in an on-site system located at the semiconductor wafer production site. In the example of aqueous ammonia, this is performed by: drawing ammonia vapor from a liquid ammonia reservoir, and scrubbing the filtered vapor with high-pH purified water (preferably ultrapure deionized water which has been allowed to equilibrate with the ammonia stream). This discovery permitted conversion of commercial grade ammonia to ammonia of sufficiently high purity for high-precision manufacturing without the need for conventional column distillation. The drawing of the ammonia vapor from the supply reservoir serves by itself as a single-stage distillation, eliminating nonvolatile and high-boiling impurities, such as alkali and alkaline earth metal oxides, carbonates and hydrides, transition metal halides and hydrides, and high-boiling hydrocarbons and halocarbons. The reactive volatile impurities that could be found in

commercial grade ammonia, such as certain transition metal halides, Group III metal hydrides and halides, certain Group IV hydrides and halides, and halogens, previously thought to require distillation for removal, were discovered to be capable of removal by scrubbing to a degree of ultrapurification which is adequate for high-precision operations. This is a very surprising discovery, since scrubber technology is traditionally used for the removal of macro-scale, rather than micro-scale, impurities. Details of such systems are described in copending US application 08/179,001 filed 1/7/94, which is hereby incorporated by reference, and in copending provisional applications 08/499,425, 08/499,414, and 08/499,413, all filed 7/7/95, and all hereby incorporated by reference.

Background: Uses of Nitric Acid in Semiconductor Processing

One of the important process chemicals is nitric acid. Nitric acid is useful for wet etching of silicon, and is also used, for example, in some recipes for chemical-mechanical polishing of interconnect metallization, and in compounds for etching various heavy metals, and for defect etching.

Innovative System and Methods for On-Site Nitric Acid Purification

The present inventors have now discovered that on-site distillation of nitric acid can be used to obtain ultrapure nitric acid for semiconductor processing.

As shown in Figure 4, the HNO_3/H_2O system has a high-bp azeotrope (68.5%wt HNO_3, nbp 122°C). In the presently preferred embodiment, the source material for distillation is provided at a concentration higher than that of the high-bp azeotrope, so that dilution does not occur during condensation. A reflux condenser is preferably used, with a continuous purge to prevent impurities from accumulating. This is performed on-site, at a semiconductor manufacturing facility, and the ultrapure chemical thus generated is routed directly, (preferably through ultraclean piping, to the point of use in a semiconductor front end.

Brief Description of the Drawing

The disclosed inventions will be described with reference to the accompanying drawings, which show important sample embodiments of the invention and which are incorporated in the specification hereof by reference, wherein:

Figure 1 is a simplified diagram of the distillation system used in the described sample embodiment of nitric acid ultrapurification.

Figure 2 shows measured data values achieved with the system of Figure 5.

Figure 3 is a block diagram of a semiconductor fabrication process which is connected to use the nitric acid produced by the purification unit of Figure 1.

Figure 4 shows a phase diagram of the H_2O/HNO_3 system.

Figure 5 shows a benchtop apparatus used to derive actual test results.

Detailed Description of the Preferred Embodiments

The numerous innovative teachings of the present application will be described with particular reference to the presently preferred embodiment (by way of example, and not of limitation), in which:

Figure 1 is a simplified diagram of an on-site distillation system used for nitric acid ultrapurification at a semiconductor manufacturing facility. Supply tank T-3 (optionally fed from tanks T-1 and T-2, to permit mixing up to concentrations above 70%) supplies nitric acid feedstock at greater than 70%wt concentration (preferably 72%wt) to the reboiler portion (R-1) of a column C-1. A top condenser CD-1 removes heat of condensation from the vapor out from the column, and aftercooler HX-1 further cools the condensate. A small top stream is vented, but this is only about 0.1% of the total vapor-phase flow. Tanks T-4 and T-5 are used alternately to dilute the product to the desired strength, and the diluted product is fed to reservoir T-6, for metering as desired to the point of use.

The condensate (product) draw is further cooled by heat exchanger HX-1. The product is then diluted, in tanks T-4 and T-5, down to the concentration (e.g. 70%wt) desired by the end-user.

Note that ultrapure water is used to dilute the acid. Typical standards for ultrapure water are a resistivity of at least about 15 megohm-cm at 25°C (typically 18 megohm-cm at 25°C), less than about 25ppb of electrolytes, a particulate content of less than about $150/cm^3$ and a particle size of less than 0.2 micron, a microorganism content of less than about $10/cm^3$, and total organic carbon of less than 100ppb.

The column will typically contain a conventional column packing to provide for a high degree of contact between liquid and gas. In one presently preferred example, the column has a packed height of approximately 3 feet (0.9 meter) and an internal diameter of approximately 7 inches (18 cm), to achieve a packing volume of 0.84 cubic feet (24 liters), and is operated at a pressure drop of about 0.3 inches of water (0.075 kPa) or less, and less than 10% flood. The packing material is preferably 8x8mm, but could alternatively be 10x10mm.

The units described up to this point may be operated in either batchwise, continuous, or semi-continuous manner. Continuous or semi-continuous operation is preferred.

The following table gives sample flows, scaled to production of one ton per day, for the system of Figure 1:

Process Flow Diagram of 1 Ton/Day 70% Nitric Acid Distillation System

Stream No	1	2	3	4	5	6	7	8
Mass. T/D	1.0000	0.1000	1.1000	0.1241	0.9759	0.9759	0.0241	1.0000
HNO3	0.6900	0.0950	0.7850	0.0850	0.7000	0.7000	0.0000	0.7000
H2O	0.3100	0.0050	0.3150	0.0391	0.2759	0.2759	0.0241	0.3000
wt%HNO3	69.00	95.00	71.36	68.50	71.73	71.73	0.00	70.00
Sp.Grav.	1.4091	1.4932	1.4190	1.2920	1.2760	1.4053	1.0000	1.3971
Rate gpm	0.1302	0.0123	0.1422	0.0176	0.1403	0.1274	0.0044	0.1313
Rate ml/m	492.83	46.51	538.33	66.70	531.13	482.26	16.73	497.06
Temp C	20	20	29.50	122	120	30	20	31.88
Spc Heat	0.617	0.485	0.605	0.620	0.608	0.608	1.000	0.615

Experimental Summary

A bench scale experiment on nitric acid distillation was carried out successfully as follows, using a 1" distillation column as shown in Figure 5. This apparatus and this experiment were designed to provide an experimental demonstration of the practicality of the full-scale apparatus of Figure 1.

The reboiler flask 2, in this sample embodiment, is heated by a 600W heating mantle 1. With this heating mantle the boil up rate is 17.4 g/min. Product is drawn between packed column 4 and condenser 5, and cooled by the following stages 7 and 8. This apparatus was operated in batch mode.

The feedstock used was 72%wt technical grade nitric acid from Fisher. (The illustrated configuration of Figure 1 can be used to provide an admixture of fuming nitric, to bring the concentration up high enough, but the presently preferred embodiment simply uses a more concentrated feedstock.)

To start up the system properly, two runs were performed: a "clean up" run was first performed using reagent grade acid, to reduce the contaminant levels in the system, and then batch distillation was performed using technical grade acid.

The table of **Figure 2** shows results from actual tests run with the bench-scale apparatus of Figure 5. This table gives measured concentrations, in parts per billion, of the various impurities listed. Note that most of the impurities were below the detection limit in the condensate.

Decomposition of Nitric Acid during Distillation.

Nitric acid does decompose during distillation, producing a noticeable amount of red brown NO_x vapor (mostly NO_2). Since the density of NO_x vapor is heavier than air but lighter than the water-nitric acid vapor, this red brown cloud tended to stay at the bottom of the condenser during the distillation experiment, and fell down into the reboiler flask after the heater was off.

The amount of this decomposition depends on the assay and the amount of the boiling acid as well as the time of distillation. The 71.4% acid was found to decompose much more readily than the 69.4 to 70.0% acid of other experiment.

Measurements of the acid balance showed that the amount of acid loss was within experimental uncertainty for all four experiments. Even for the first experiment with the most obvious decomposition qualitatively, the apparatus was dry at the start and most of the 2% acid loss should remain in the wetted packed column. Consequently, only a small portion of the acid loss would be due to decomposition.

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Even though the decomposition rate is very low, the decomposed products may accumulate; thus in a continuous process the red-brown cloud of NO_x vapor will eventually fill up the condenser and continuously vent to the scrubber.

<u>Integrated Circuit Fabrication</u>

Figure 3 is a block diagram of a semiconductor fabrication process which is connected to use the nitric acid produced by the purification unit of Figure 1.

In the flow shown, incoming wafers are thoroughly cleaned and tested ("Wafer preparation"). Nitric acid may be used at this step to remove metallic surface contaminants. Next ("Isolation and Well formation") the n-wells and/or p-wells are formed (for a CMOS process), together with the field isolation regions (typically LOCOS or some variant thereof). Next a VT implant is performed, a sacrificial oxide is grown and stripped, a gate oxide is grown, an insulated gate is formed (e.g. of a silicided polysilicon on the gate oxide) and patterned, and source/drain regions are formed (typically in multiple steps, to provide LDD or graded-drain structures). A first interlevel dielectric ("ILD") is now formed, and a second polysilicon (or polycide) layer is now deposited and patterned. A second ILD is now formed and patterned, and a first metallization layer ("Metal-1") is now formed and patterned. A third ILD is now formed and patterned, and a second metallization layer ("Metal-2") is now formed and patterned. CMP may be used to planarize the upper ILD layers above or beneath the metal layers. Finally a protective overcoat is deposited, and patterned to expose contact pad locations.

<u>Modifications and Variations</u>

As will be recognized by those skilled in the art, the innovative concepts described in the present application can be modified and varied over a tremendous range of applications, and accordingly the scope of patented subject matter is not limited by any of the specific exemplary teachings given.

For another example, the disclosed innovative techniques are not strictly limited to manufacture of integrated circuits, but can also be applied to manufacturing discrete semiconductor components, such as optoelectronic and power devices.

For another example, the disclosed innovative techniques can also be adapted to manufacture of other technologies where integrated circuit manufacturing methods have been adopted, such as in thin-film magnetic heads and active-matrix liquid-crystal displays; but the primary application is in integrated circuit manufacturing, and applications of the disclosed techniques to other areas are secondary.

It should also be noted that piping for ultrapure chemical routing in semiconductor front ends may include in-line or pressure reservoirs. Thus references to "direct" piping in the claims do not preclude use of such reservoirs, but do preclude exposure to uncontrolled atmospheres.

CLAIMS

What is claimed is:

1. An on-site subsystem, in a semiconductor device fabrication facility, for providing ultra-high-purity nitric acid to a semiconductor manufacturing operation, comprising:
   a source of nitric acid at a concentration greater than 68%wt;
   a reflux distillation column connected
      to receive nitric acid from said source at a heated lower point on said column,
      to provide a flow of nitric acid condensate from an upper point on said column, and
      to provide a purge flow which averages at least 4% of the volume of said flow of nitric acid condensate, from a purge point on said column which is below said upper point on said column;
   a reservoir connected to receive said flow of nitric acid condensate;
   a piping connection which routes said nitric acid condensate from said reservoir to points of use in the semiconductor device fabrication facility.

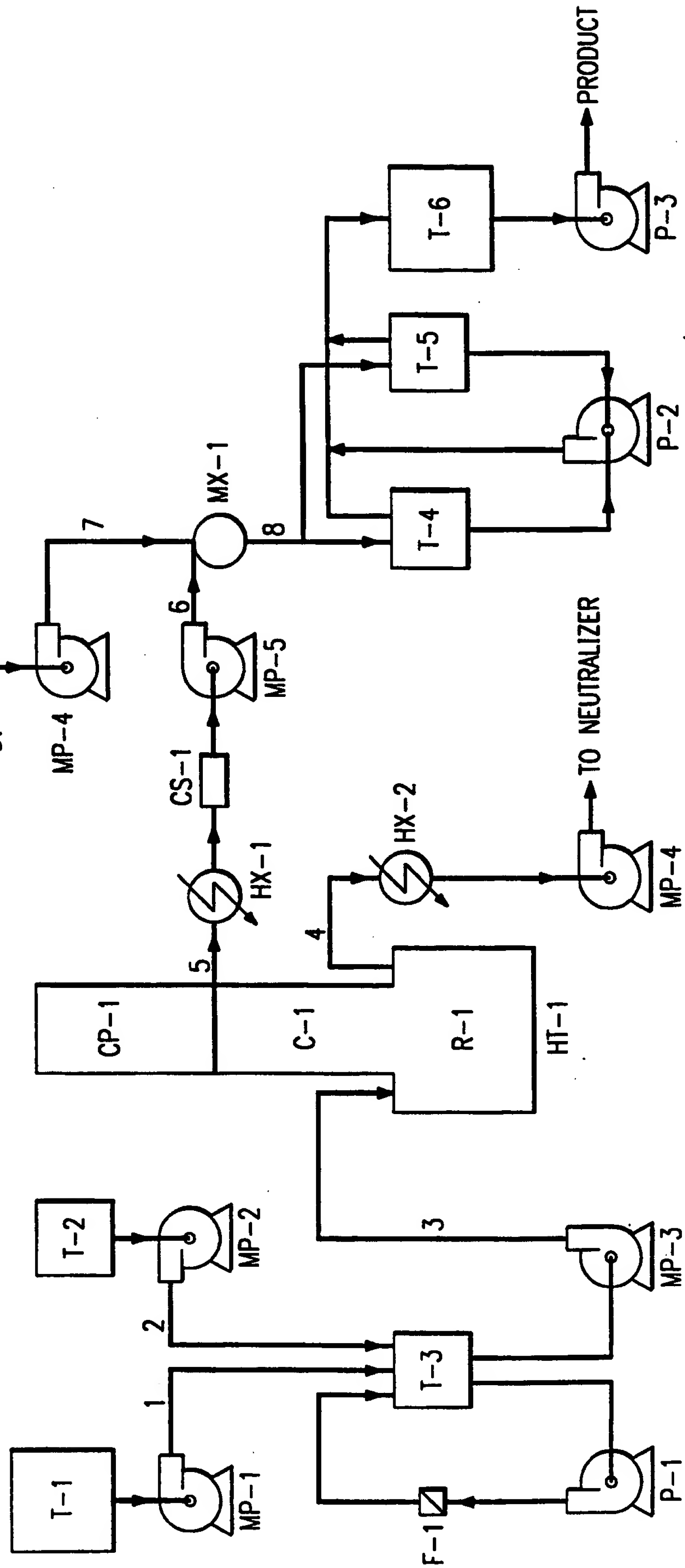

PRODUCT
T-6
P-3
T-5
P-2
MX-1
7
8
T-4
DI
MP-4
6
MP-5
TO NEUTRALIZER
CS-1
HX-2
HX-1
4
MP-4
5
CP-1
C-1
R-1
HT-1
T-2
MP-2
3
MP-3
2
T-3
1
T-1
MP-1
F-1
P-1

FIG. 1

	Clean Up with Reagent Grade Acid				Batch Distillation of Technical Grade Acid				
	1st Dist.	1st Dist.	2nd Dist.	2nd Dist.	Tech Gr.	1st Cut	2nd Cut	3rd Cut	Pot Liq.
Date Ana	04/09/96	04/10/96	04/09/96	04/10/96	04/10/96	04/09/96	04/09/96	04/09/96	04/09/96
Sample	04081715	04081715	04081725	04081725	50-13	04091130	04091200	04091215	04091400
Element	(ppb found)	(ppb found)	(ppb found)	(ppb found)	(ppb found)	(ppb found)	(ppb found)	(ppb found)	(ppb found)
Na	22.56	18.24	83.1	79.2	137.97	<1	<1	4.11	122.7
Mg	<1	<1	4.81	4.66	<1	<1	<1	<1	37.03
Al	<1	<1	<1	<1	<1	<1	<1	<1	4.02
P	355.9	<50	140.6	<50	<50	<50	<50	<50	<50
K	<1	<1	<1	<1	<1	<1	<1	<1	<1
Ca	<1	<1	<1	<1	<1	<1	<1	<1	<1
V	<1	<1	<1	<1	<1	<1	<1	<1	<1
Cr	57.53	51.18	<2	<2	<2	<2	<2	<2	26.71
Mn	51.24	51.94	<1	<1	<1	<1	<1	<1	<1
Fe	1152	1134	25.8	19.4	<2	<2	<2	<2	<2
Ni	313.2	319.4	<2	<2	<2	<2	<2	<2	15.57
Co	3.48	<1	<1	<1	<1	<1	<1	<1	<1
Cu	5.05	<1	<1	<1	<1	<1	<1	<1	1.48
Zn	83.41	82.35	<1	<1	<1	<1	1.07	<1	20.53
Me	<0.5	2.79	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Cd	<2	<2	<2	<2	<2	<2	<2	<2	<2
Ba	<2	<2	<2	<2	<2	<2	<2	<2	<2
Pb	<5	<5	<5	<5	<5	<5	<5	<5	<5

FIG. 2

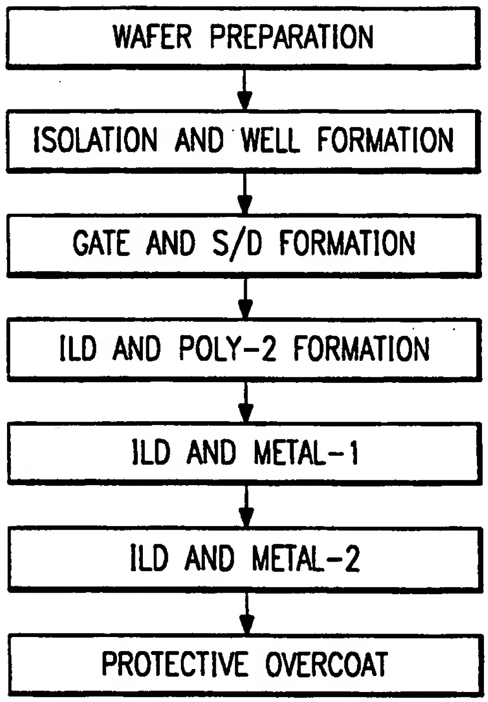
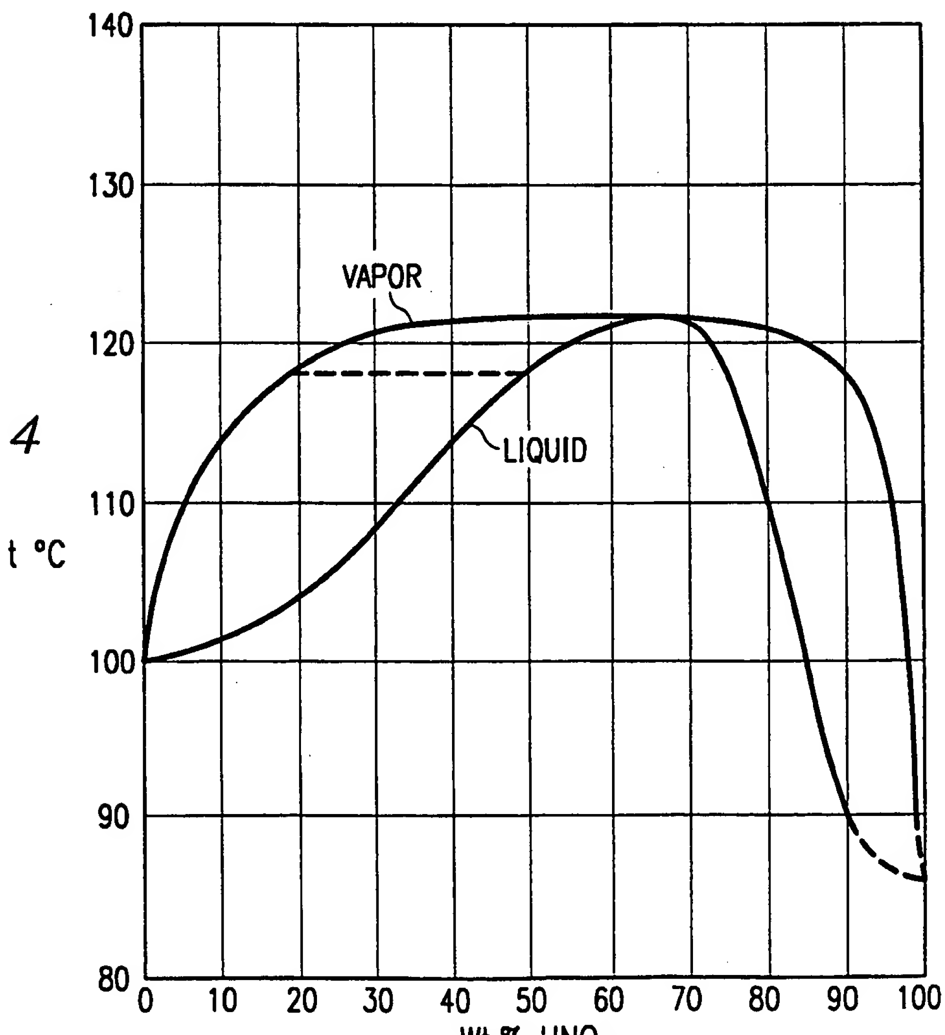


FIG. 3

FIG. 4



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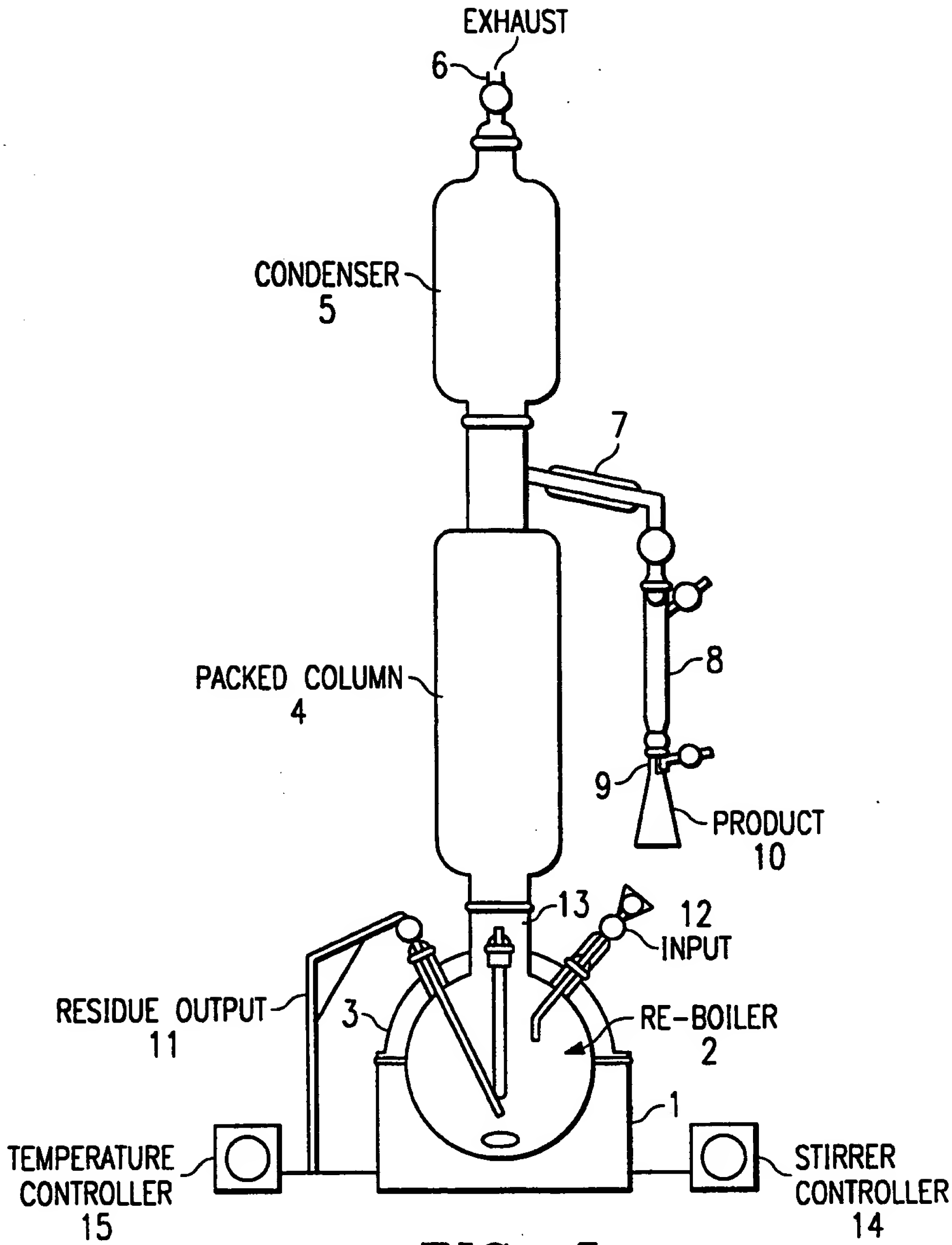
EXHAUST
6
CONDENSER
5
7
PACKED COLUMN
4
8
9
PRODUCT
10
13
12
INPUT
RESIDUE OUTPUT
11
3
RE-BOILER
2
1
TEMPERATURE
CONTROLLER
15
STIRRER
CONTROLLER
14

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/09215

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B08B 7/04; B01D 1/00, 3/14,3/02,3/00; C01B 7/19, 7/07; F26B 7/00
US CL : 134/12; 423/484,488; 202/158,161,172,200; 159/47.1; 203/31,33,34
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 134/12; 423/484,488; 202/158,161,172,200; 159/47.1; 203/31,33,34

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, CAS WPIDS
SEARCH TERMS: HF, SEMICONDUCTOR, DISTIL?, EVAPOR?, NITRIC, ACID, REGENERAT?

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	US, A, 5,500,098 (BROWN ET AL.) 19 MARCH 1996(19.03.96), SEE COLUMN 4, LINES 46-68.	1
Y,P	US, A, 5,496,778 (HOFFMAN ET AL.) 05 MARCH 1996 (05.03.96), SEE ENTIRE DOCUMENT.	1
Y	US, A, 5,362,469 (SESEKE-KOYRO ET AL.) 08 NOVEMBER 1994 (08.11.94) COLUMN 3, LINES 9-14 AND COLUMN 4 LINES 48-57.	1
Y	US, A, 5,346,557 (ITO ET AL.) 13 SEPTEMBER 1994 (13.09.94), SEE FIG. 1 AND COLUMN 5, LINES 5-45.	1
Y	US, A, 5,288,333 (TANAKA ET AL.) 22 FEBRUARY 1994 (22.02.94), SEE ENTIRE DOCUMENT.	1

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

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Date of the actual completion of the international search

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,164,049 (CLARK ET AL.) 17 NOVEMBER 1992 (17.11.92), SEE ENTIRE DOCUMENT.	1
A	US, A, 4,980,032 (DOBSON ET AL.) 25 DECEMBER 1990 (25.12.90), SEE FIGURE 1.	1
Y	US, A, 4,952,386 (DAVISON ET AL.) 28 AUGUST 1990 (28.08.90), SEE COLUMN 2, LINES 23-60.	1
A	US, A, 4,929,435 (BOGHEAN ET AL.) 29 MAY 1990 (29.05.90), SEE ABSTRACT.	1
Y	US, A, 4,828,660 (CLARK ET AL.) 09 MAY 1989(09.05.89), SEE COLUMN 7, LINES 1-68 AND COLUMN 8, LINES 1-68.	1
A	US, A, 4,756,899 (JENCZEWSKI ET AL.) 12 JULY 1988 (12.07.88), SEE ABSTRACT.	1
A	US, A, 4,144,092 (KREPLER) 13 MARCH 1979 (13.03.79.), NOTE ABSTRACT.	1